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# REDUCTION AND PHENOL ACID DEPOLYMERIZATION OF WESTERN U.S. OIL SHALE KEROGEN

By

J. Solash, D. C. Cronauer, and T. P. Kobylinski
Gulf Research & Development Company,
P. O. Drawer 2038, Pittsburgh, Pennsylvania 15230

## INTRODUCTION

The chemical structure of U.S. Western oil shale kerogen is not known with certainty. Many structure studies employed strong oxidants to degrade kerogen (1-4). Acidic products are isolated and analyzed. In most cases, relatively small amounts of material are analyzed. Structural inferences from analysis of small quantities (generally less than 20% of kerogen) of degraded material are apt to be misleading.

The literature is in conflict regarding even basic structural features of kerogen. Yen and coworkers have used X-ray analysis to deduce that kerogens contain very little aromatic material (5). However, $^{13}C$ CP/MAS nmr measurements show that Western kerogens are 20-30% aromatic (6,7). The structure of nitrogen containing moieties is also in doubt. It has been suggested (8) that tetrapyrroles in kerogen pyrolyze to yield pyridines, quinolines, and other classes of nitrogeneous compounds found in shale oil. No quantitative data were given. Pyrolysis of simple pyrroles was found to give low yields of pyridines (9). Pyridines and quinolines are the major nitrogen-containing species in distillate shale oils.

Our approach has been to attempt to degrade Western U.S. oil shale kerogen under mild conditions. There has been a report of reducing kerogen using dissolving metals (10). Jones and Dickert reported that treating Colorado oil shale kerogen with lithium aluminum hydride, HI, or lithium in ethylene diamine were all ineffective in increasing kerogen solubility (10). Interestingly, HI has been reported to convert kukersite to 100% ether and benzene solubles (11). No data were reported on the possible extent of reduction with lithium in ethylene diamine.

We would like to report our results of treating kerogen with several well-known reagents. We decided to reinvestigate reductively alkylating kerogen using sodium in hexamethylphosphoric triamide (Na/HMPA). This reagent has been reported to be a superior medium to produce solvated electrons (12). Na/HMPA is capable of reducing isolated double bonds (13); reducing the solvent or adding an electron transfer agent to the substrate can be avoided using Na/HMPA (14). There is a rich literature dealing with similar reduction of coal and model compounds (15-18). Treating kerogen with Na/HMPA and a variety of alkylating agents resulted in only small increases in solubility. Treating kerogen with known ether and ester cleavage reagents ($FeCl_3/Ac_2O$; $Me_3SiCl/NaI$) resulted in very little increase in kerogen solubility. Kerogen is rapidly but incompletely oxidized by trifluoroperoxyacetic acid (TFPA). The oxidized products show evidence of pyridines and quinolines. Phenol-toluenesulfonic acid treatment results in solubilizing large fractions of kerogen.

## EXPERIMENTAL

### General Methods

The kerogens used in this study were derived from Colorado oil shale. The oil shales used are: R351, a 25 gal/ton (gpt) shale; Rio Blanco, a 22 gpt shale; and Hazen, a 52 gpt pretreated shale. These oil shales were all mined from the Gulf C-a tract. R-351 is a Mahogany Zone oil shale of unknown geographic origin. The Rio Blanco and Hazen samples were both from the MDP-1 core; Rio Blanco is a core composite sample while Hazen is a homogeneous G-level oil shale sample. The Hazen sample was beneficiated by gravity methods (1.60 sp. gr. float) prior to our treatment. Minerals were removed from the oil shales by sequential HCl then HF treatment. Bitumen was removed from the kerogens by extracting with benzene-methanol (7:3). The elemental analysis of the three kerogens used is presented in Table I. Others at our laboratories are investigating the nature of residual mineral matter in kerogen after beneficiating in various ways.

Elemental analyses were determined by Microanalysis Inc., Wilmington, Delaware; oxygen was directly determined by a modified Unterzaucher technique. IR spectra were recorded on a Digilab Model 15C interferometer using KBr pellets. NMR spectra were recorded on a Varian XL-200.

TABLE I

ELEMENTAL ANALYSES OF KEROGEN CONCENTRATES

| Sample | Elemental Analysis, wt% | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | S | O | F | Cl | Ash |
| R351 | 69.35 | 8.75 | 1.61 | 4.84 | 5.90 | 1.16 | ---- | 6.44 |
| Rio Blanco | 65.12 | 8.15 | 2.10 | 4.59 | 10.21 | 0.77 | 1.03 | 11.03 |
| Hazen | 65.40 | 8.79 | 2.05 | 3.24 | 5.37 | 1.49 | 0.22 | 13.57 |

Dissolving Metal Reduction

A typical experiment follows: a 100 ml round bottom flask, equipped with pressure equalizing addition funnel, efficient condenser, and gas addition tube was used. The apparatus was oven dried, assembled hot, and allowed to cool under dry $N_2$. The flask was charged with 15 ml of freshly distilled HMPA. Sodium (about 1.5 g) was freshly cut into small pieces. Several pieces of sodium were added to the HMPA with stirring. After several minutes, the solution turned blue. About 1 g of kerogen was added; 5 ml of HMPA were used to rinse any kerogen adhering to the sides of the flask. The blue color disappeared upon adding kerogen. After solvated electrons reappeared, the addition funnel was charged with the calculated quantity of quencher (methanol or alkyl iodides). The quencher was added dropwise until the blue color was removed; when solvated electrons reappeared more quencher was added. Sodium was added as required. The quantity of quencher was calculated on the basis of the aromatic content (assume fa = .25) and the oxygen content. After all quenching agent was added, the mixture was poured into 50 ml of water and filtered. The solids were washed with large volumes of water, dried in vacuo (85°C, 24-48 hr, 300-400 torr), and weighed. The solids were then Soxhlet extracted with toluene and submitted for elemental analysis. Incorporated $^{13}C$ (from ethyl iodide-1-$^{13}C$) was determined by Global Geochemistry, Inc., Canoga Park, California, using a combustion method.

Phenol-p-Toluene Sulfonic Acid Depolymerization

The kerogens were treated with phenol and tosyl acid according to literature methods (24). After reacting, excess phenol was removed by steam distilling. The products were filtered, washed with water, and dried in vacuo. The products were then Soxhlet extracted with toluene, methanol, and finally pyridine. Extracts were isolated, weighed, and analyzed as outlined in the text. Product recoveries are outlined in Figure 1. For instance, for the Rio Blanco (RB) kerogen, 3.87 g of solids were recovered from 2.00 g of starting kerogen (193% yield). From the recovered (phenolated) product, 46% was soluble in toluene.

The toluene soluble products from each reacted kerogen were subjected to SARA analysis (saturates, aromatics, resins, asphaltenes). The Rio Blanco toluene solubles gave almost 91% asphaltenes. The Hazen kerogen toluene solubles were almost 81% asphaltenes. The Hazen toluene solubles were more difficult to handle; 14.5% of the material was unrecovered from the chromatographic column.

## RESULTS AND DISCUSSION

Reductive Alkylation

The kerogens described in the experimental section were reductively alkylated by continually quenching the intermediate anions. The method requires that the dark blue solution (solvated electrons) be stoichiometrically quenched with alkylating agent. When the dark blue solution reappears, more alkylating agent is added. The results of reductively alkylating three kerogens with methanol (protonate) and ethyl-, butyl-, and octyliodide are presented in Table II.

Table II presents the recovery and elemental analysis data of the solids recovered after reductively alkylating. In a number of cases, the recovery of material was greater than 100% based on starting kerogen. Using the elemental analysis data in Tables I and II, we calculated the number of alkyl (or proton) groups added to the kerogens. The R351 and Rio Blanco kerogens incorporated more protons and alkyl groups than the Hazen kerogen. In two experiments (Table II, Runs 6 and 12) we used $^{13}C$ labelled ethyl iodide as alkylating agent and measured incorporated $^{13}C$ in the product solids. We found that the Rio Blanco kerogen incorporates almost twice the number of ethyl groups as the Hazen kerogen (2.44 vs. 1.25 ethyl groups/100 atoms C) based on $^{13}C$ labelling data. This compares fairly well with the elemental analysis data in Table II (Runs 6 and 12).

While we can alkylate kerogen, the alkylated products were only slightly (<5%) soluble in toluene. These results must be compared to those found for reductive alkylates of coal (15,16). Reductively alkylating coal generally results in very large increases in benzene or toluene solubility of the alkylated coal product. Dissolving metals are very effective for reductively cleaving many kinds of ethers and esters. Some carbon-carbon bonds are also cleaved by reductive alkylation.

The lack of increased alkylated-kerogen solubility implies that ether linkages are not important in holding kerogen together. To confirm this, kerogen was treated with $FeCl_3/Ac_2O$ (19) and $(H_3C)_3$-SiCl/NaI (20). These known ether-cleavage reagents failed to increase the toluene solubility of our kerogens. Ethers and ester linkages can be ruled out as important crosslinks of kerogen "monomers".

TABLE II

ELEMENTAL ANALYSES FOR Na/HMPA TREATED KEROGENS

| Sample | Elemental Analysis, wt% C | H | N | S | O | AA[a] | #Gp/ 100 C | Recovery |
|---|---|---|---|---|---|---|---|---|
| R351 (1) | 65.35 | 8.97 | 2.94 | -- | -- | M | 14[b] | 97.6% |
| (2) | 71.22 | 9.4 | 12.34 | 2.59 | 9.61 | O | 3.3 | 105 |
| Rio Blanco | | | | | | | | |
| (3) | 63.79 | 8.40 | 2.15 | 4.32 | 11.45 | M | 8 | 93.5 |
| (4) | 64.95 | 8.36 | 2.50 | 5.88 | 8.75 | M | 4 | 83.5 |
| (5) | 64.08 | 8.37 | 2.34 | 2.14 | -- | E | 2.8 | 88.3 |
| (6) | 66.67 | 8.82 | 2.34 | 3.04 | 7.95 | E-$^{13}$C | 3.6 | 97.4 |
| (7) | 65.76 | 8.75 | 2.35 | 3.60 | 8.94 | B | 4.4 | 106 |
| (8) | 66.61 | 8.95 | 2.45 | 2.31 | 8.24 | B | 4.9 | 95 |
| Hazen | | | | | | | | |
| (9) | 64.96 | 8.75 | 2.48 | 1.51 | 5.75 | M | 0.0 | 91.8 |
| (10) | 62.45 | 7.95 | 2.30 | 2.54 | 9.10 | M | -8 | 88.7 |
| (11) | 66.24 | 9.01 | 3.40 | 1.93 | -- | E | 0.8 | 108 |
| (12) | 65.61 | 8.89 | 2.12 | 2.66 | 5.10 | E-$^{13}$C | 0.4 | 97 |
| (13) | 63.54 | 8.85 | 3.00 | 1.79 | -- | B | 2.7 | 108 |

a. AA = alkylating agent; M = methanol, E = ethyl iodide, B = butyl iodide, O = octyl iodide.

b. All entries in this column refer to the calculated number of alkyl groups incorporated per 100 atoms C of substrate (see text for details).

TFPA Treatment of Kerogens

We treated our kerogen with TFPA. We found that all kerogens lost weight after exposure to TFPA but to varying extents. These results will be published elsewhere (21).

Phenol-Tosyl Acid Depolymerization

The use of phenol-p-toluenesulfonic acid to dissolve coal is well-known (22-25). This method apparently has not been applied to oil shale kerogens (26).

In Figure 1, an outline of the product recovery results from phenol-tosyl acid treatment of kerogen is shown. Product recoveries are high (183-193%). Kerogen is much more reactive toward phenol than is coal (23,24). The recovered products were sequentially extracted with toluene, methanol, and pyridine. The extracts were isolated and weighed. As shown in Figure 1, the depolymerized products are 42-46% soluble in toluene. This wt% solubility in toluene assumes a fairly uniform distribution of phenol in all the products. We will confirm this assumption using labelled phenol. In Tables III and IV are shown the results of elemental analyses and some molecular weight measurements on the toluene-soluble material from depolymerized Rio Blanco and Hazen kerogen.

The results shown in Tables III and IV reveal some interesting features of these kerogens. The elemental analyses of the extracts from both kerogens are remarkably similar. There is a partitioning of nitrogen and sulfur heteroatoms among the solvents according to solvent polarity. The oxygen content of the extracts remains approximately constant. The H/C atomic ratio of the various solvent extracts also does not vary much (H/C = 1.00 $\pm$ .08) for the Rio Blanco kerogen extracts (Table III). The H/C average value of 1.00 shows that much less hydrogen is present in the products. This is consistent with large amounts of incorporated phenol. The H/C atomic ratio varies more for the solvent extracts of phenol-reacted Hazen kerogen; H/C is 0.86 for toluene solubles, 1.0 for methanol solubles, and 1.26 for pyridine solubles. If we assume that the toluene-soluble fraction of the Hazen kerogen should have an oxygen content of about 5.4% (assume uniform elemental distribution among solvent extracts), then 11.6% oxygen found represents oxygen from incorporated phenol. The amount of phenol incorporated in the toluene solubles on this basis is 33% for the Rio Blanco kerogen ([12-6.4] x [$\frac{94}{16}$]) and 36% for the Hazen kerogen ([11.6 - 5.4] x [$\frac{94}{16}$]).

Large quantities of incorporated phenol are also evident from the $^1$H and $^{13}$C spectra of the toluene solubles (Figure 2). The sharp bands in the aromatic regions of the $^1$H and $^{13}$C spectra are due to substituted phenol moieties. The $^{13}$C spectrum integral can be used to calculate how

much phenol was incorporated in the Rio Blanco toluene solubles. Using the data shown in Figure 2 (first correcting for small amounts of residual toluene), we calculate that the toluene solubles from the Rio Blanco depolymerized kerogen contain about 46 wt% (incorporated) phenol.

TABLE III

DEPOLYMERIZATION OF RIO BLANCO OIL SHALE KEROGEN VIA PHENOL-TsOH

| Kerogen | Soxhlet[b] Solvent | Elemental Analysis, wt% C | H | N | S | O | MW[a] |
|---|---|---|---|---|---|---|---|
| Unreacted | | 64.5 | 8.4 | 2.1 | 5.6 | 6.4 | |
| C-a, Rio Blanco | Tol. Sol. | 78.4 | 6.0 | 0.13 | 1.7 | 12.0 | 272(VPO) 334(GPC) |
| | MeOH Sol. | 73.0 | 6.1 | 1.3 | 5.2 | 13.3 | 494(VPO) 343(GPC) |
| | Pyridine Sol. | 77.2 | 6.7 | 2.3 | 2.9 | 10.0 | |

a. Wt. Aver. MW by GPC for Tol. Extr. and MeOH Extr. are less than 1000.
b. Solvent soluble fraction of crude, isolated phenol kerogen product.

TABLE IV

DEPOLYMERIZATION OF HAZEN OIL SHALE KEROGEN VIA PHENOL-TsOH

| Kerogen | Soxhlet[b] Solvent | Elemental Analysis, wt% C | H | N | S | O | MW[a] |
|---|---|---|---|---|---|---|---|
| Unreacted | | 65.4 | 8.8 | 2.1 | 3.2 | 5.4 | |
| C-a, Hazen | Tol. Sol. | 80.6 | 5.8 | 0.25 | 1.5 | 11.6 | 276(VPO) 370(GPC) |
| | MeOH Sol. | 73.4 | 6.1 | 1.2 | 4.1 | 12.8 | |
| | Pyridine Sol. | 61.2 | 6.4 | 2.8 | 8.0 | 16.3 | |

a. Wt. Aver. MW by GPC for Tol. Extr. and MeOH Extr. are less than 1000.
b. Solvent soluble fraction of crude, isolated phenol kerogen product.

The data in Tables III and IV also reveal that individual "monomeric" units of oil shale kerogen are of very low molecular weight. For instance, the major toluene-soluble fraction of each depolymerized kerogen has an average molecular weight of about 300-400. If almost half the carbons of toluene-soluble depolymerized Rio Blanco kerogen are from reagent phenol, then the molecular weights of "monomeric" kerogen units shown in Table III should be decreased by one or two incorporated phenol molecules (94-188 units).

The molecular weight data for the toluene-soluble fractions of both depolymerized kerogen products was confirmed by field ionization mass spectroscopy (FIMS). A FIMS spectrum for the depolymerized Rio Blanco kerogen toluene solubles is shown in Figure 3. The number average molecular weight calculated from Figure 3 is 401. Figure 3 shows that much of the ion intensity is concentrated in a relatively small number of peaks. The FIMS data cannot be compound-class analyzed using hydrocarbon classes only since the toluene solubles for this fraction contain about 12% oxygen. We do not want to assume that all oxygen in the toluene solubles is from incorporated phenol (the data do not support this assumption). Thus, assigning our FIMS data to specific hydrocarbon classes is not possible. We are applying low voltage-high resolution mass spectroscopy methods to these samples. We are also further fractionating our depolymerized samples to allow for simpler structure analysis.

The elemental analysis data (Tables III and IV) and the nmr spectra (Figure 2) of the depolymerized kerogen are surprising. The alkyl carbon portion of the $^{13}C$ nmr spectrum is dominated by long chain saturates (chain length $\approx$15 carbons). There is little saturated cycloalkyl carbon present. Recently it was proposed that kerogens are composed primarily of saturated condensed cycloalkanes (27). The depolymerized products also appear to be "too aromatic". For instance, on the basis of the $^{13}C$ nmr spectrum, we calculated that the depolymerized Rio Blanco kerogen toluene solubles had 46 wt% incorporated phenol. The atomic H/C ratio of the original Rio Blanco kerogen (Table I) is 1.49. After correcting for incorporated phenol (and residual toluene) by nmr, the calculated atomic H/C for the toluene-soluble Rio Blanco products is 0.95. This is much lower than

Figure 1

## PHENOL-TsOH REACTION WITH KEROGEN

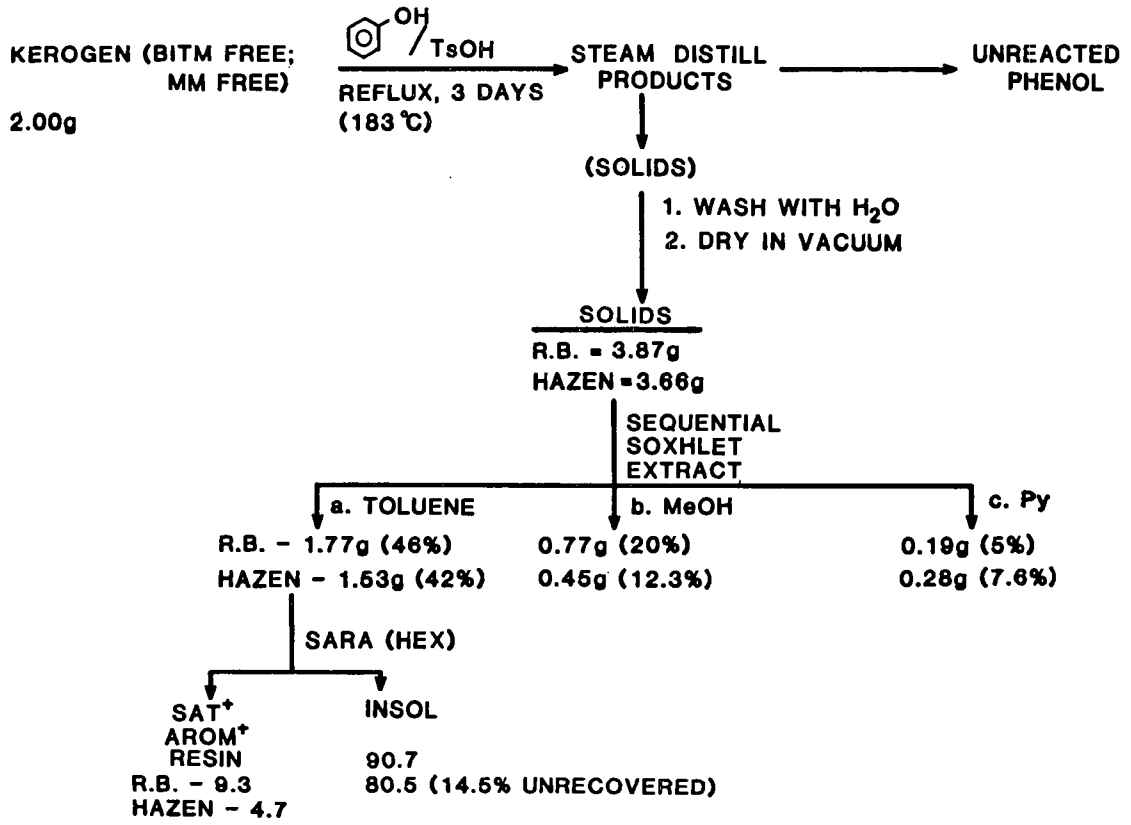
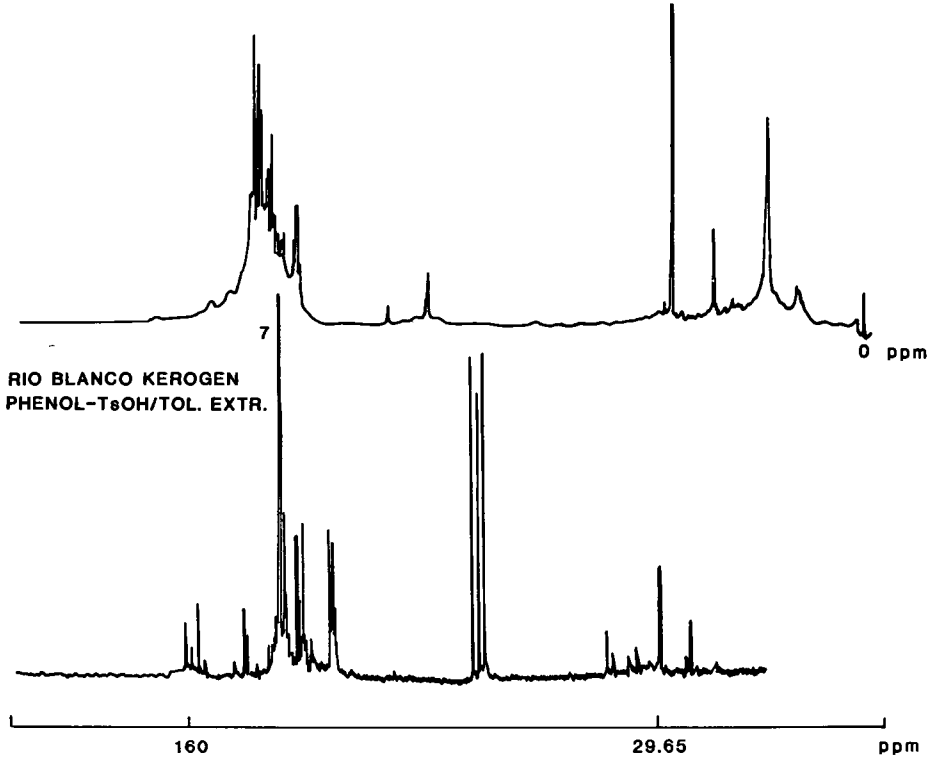


Figure 2
NMR Spectra of Depolymerized Rio Blanco
Kerogen; Toluene Solubles.
Top: $^{1}H$-NMR Spectrum.
Bottom: $^{13}C$-NMR Spectrum



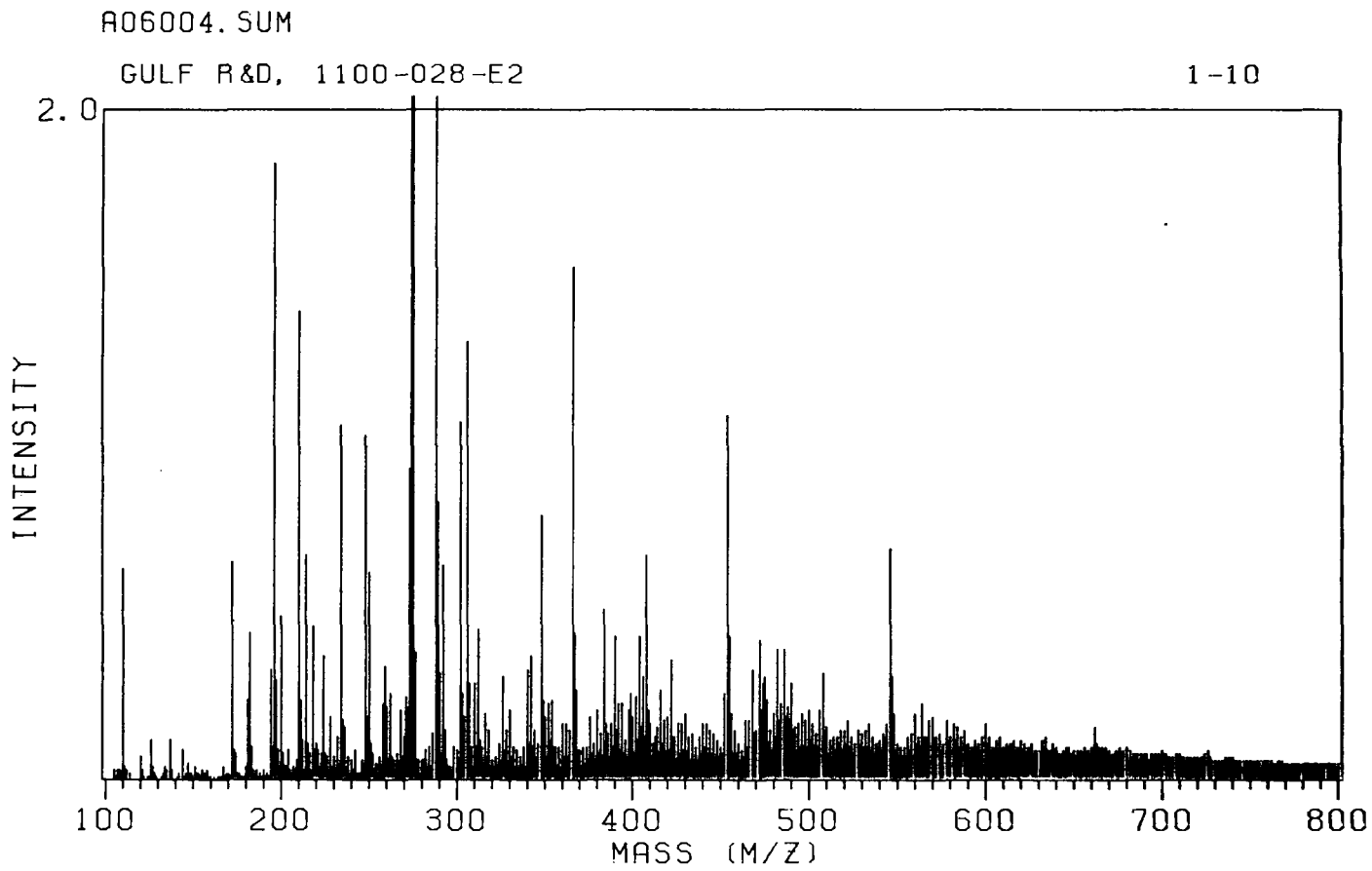



Figure 3. FIMS spectrum of depolymerized Rio Blanco kerogen-toluene solubles.

expected for the least polar fraction from a Western U.S. kerogen. We are currently engaged in studying the effect of phenol-tosyl acid on model compounds.

The Rio Blanco kerogen (MDP-1 core composite) is more reactive toward reductive alkylation and phenol depolymerization than the Hazen kerogen. It is tempting to suggest that the reactivity differences are structure related. However, if this were true, then these differences should be reflected in the soluble reaction products. We cannot adequately detect such differences solely with instrumental methods. We are currently engaged in performing several additional experiments. First, we are performing a depolymerization using $^{13}C$-labelled phenol. This will permit an accurate mass balance to be made. Second, we have methylated the toluene-soluble products from unlabelled phenol depolymerization. The methylated fractions should be more easily fractionated by chromatography. Analysis of the chromatographic fractions should be simpler.

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## LITERATURE CITED

(1) Burlingame, A. L., and Simoneit, B. R., Nature, 222, 741 (1969).
(2) Robinson, W. E., Heady, H. H., and Hubbard, A. B., Ind. Eng. Chem., 45, 788 (1953).
(3) Robinson, W. E., and Lawlor, D. L., Fuel, 40, 375 (1961).
(4) Ishiwatari, R., and Machihara, T., Geochim. Cosmochim. Acta, 46, 825 (1982).
(5) Yen, T. F., ACS, Div. Fuel Chem., Preprints, 19, 109 (1974); Young, D. K., and Yen, T. F., Geochim. Cosmochim. Acta, 41, 1411 (1977).
(6) Resing, H. A., Garroway, A. N., and Hazlett, R. N., Fuel, 57, 450 (1978).
(7) Miknis, F. P., Maciel, G. E., and Bartuska, V. J., Org. Geochem., 1, 169 (1979); Miknis, F. P., Szenerengi, N. M., and Maciel, G. E., Fuel, 61, 341 (1982).
(8) Jackson, L. P., and Decora, A. W., ACS Div. Fuel Chem., Preprints, 20 (2), 147 (1975).
(9) Jacobsen, I. A., Jr., Heady, H. H., and Dinneen, G. U., J. Phys. Chem., 62, 1563 (1958); Jacobsen, I. A., Jr., and Jensen, H. B., J. Phys. Chem., 66, 1245 (1962); Jacobsen, I. A., Jr., and Jensen, H. B., J. Phys. Chem., 68, 3068 (1964).
(10) Jones, D. G., and Dickert, J. J., Jr., Amer. Inst. Chem. Eng., Symp. Ser., 61 (54), 33 (1965).
(11) Randsepp, Kh. T., Izvest. Akad. Nauk SSSR, Otdel. Tekh. Nauk, (3), 130 (1954); in Chem. Abstr., 49, 4969c (1955).
(12) Fraenkel, G., Ellis, S. H., and Dix, D. T., J. Amer. Chem. Soc., 87, 1406 (1965).
(13) Whitesides, G. M., and Ehmans, E. J., J. Org. Chem., 35, 3565 (1970).
(14) a. Franz, J. A., and Skiens, W. E., Fuel, 57, 502 (1978); b. Garst, J. F., Accts. Chem. Res., 4, 400 (1971).
(15) Ouchi, K., Hirano, Y., Makabee, M., and Itoh, H., Fuel, 59, 751 (1980).
(16) Sternberg, H. W., and Delle Donne, C. L., Fuel, 53, 172 (1974); and previous papers in this series.
(17) Collins, C. J., Homback, H. P., Maxwell, B., Woody, M. C., and Benjamin, B. M., J. Amer. Chem. Soc., 102, 851 (1980).
(18) Birch, A. J., Hinde, A. L., and Radom, L., J. Amer. Chem. Soc., 103, 284 (1981); also see same authors, ibid. 102, 6430, 4074, 3370 (1980) and 100, 4681 (1978).
(19) Ganem, B., and Small, V. R., Jr., J. Org. Chem., 39, 3728 (1974).
(20) Olah, G. A., Narang, S. C., Gupta, B. G. B., and Malhotra, R., J. Org. Chem., 44, 1247 (1979).
(21) Solash, J., Cronauer, D. C., Kobylinski, T. P., Young, D. C., Painter, P. C., and Synder, R. W., *submitted* for publication.
(22) For a review: Larsen, J. W., and Kuemmerle, E. W., Fuel, 55, 162 (1976).
(23) Heredy, L. A., and Neuworth, M. B., Fuel, 41, 221 (1962); Heredy, L. A., Kostgo, A. E., and Neuworth, M. B., Fuel, 42, 182 (1963); 43, 414 (1964); 44, 125 (1965).
(24) Ouchi, K., Imuta, K., and Yamashita, Y., Fuel, 52, 160 (1973); 44, 29 (1965); 44, 205 (1965).
(25) Yurum, Y., and Yiginsu, I., Fuel, 60, 1027 (1981); Yurum, Y., Fuel, 60, 1031 (1981).
(26) Transalkylating of fossil fuels substrates, including petroleum resids has been studied by M. Farcaisu (Presentation at Fuel Science Meeting, Gordon Conferences, 1982). The transalkylating reagent used was xylene in the presence of a strong acid catalyst.
(27) Bandurski, E., Energy Sources, 6, 47 (1982).